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8

XXVII. *Note on the Occurrence of Traces of the Heavy Metals in the Sandstones of the Moray Firth Basin.* By WM. MACKIE, M.A., M.D.

(Read 20th March 1902.)

SOME months ago in an inquiry into the possible cause of the preecipitation of peroxide of manganese in the dark stains seen in some sandstones, and typically at Newton in the U.O.R. division of the Elgin sandstones, I was surprised to find that in addition to the oxide of manganese these stained areas showed notable traces of copper as well as of nickel and cobalt. Other small nodules occurring in a Triassic sandstone overlying the Rosebrae division of the U.O.R. rocks near the Old Hospital Quarry were found to contain, in association with a relatively greater proportion of the manganese oxide, very much larger proportions of the bases indicated— CuO $\cdot 12\%$, oxides of nickel and cobalt $\cdot 69\%$, with the addition of $1\cdot 68\%$ of lead calculated as PbO_2 or PbS . As these occurrences were ascribed to secondary local infiltration it was naturally inferred that the surrounding sandstones would if examined probably also show traces of the same metals. Accordingly determinations of the amount of copper oxide, and also of the nickel and cobalt oxides conjointly in a series of specimens (sixteen in all), ranging in time from the L.O.R. of Tarradale, Culloden, and Spey Bridge through the U.O.R. division to the Triassic rocks of Cuttishillock, Spynie and Cummingston have been made, and in not a single specimen has the copper oxide been found absent, while of the nickel and cobalt, traces of at least one and not improbably both have been found in every instance. The difficulty of effecting a separation with such minute quantities of material has necessarily prevented individual determination in all cases; but the presence of both of these metals in the manganese areas at least has been definitely ascertained. The residues in a number of the determinations have been preserved, and from the aggregate it is intended to ascertain the average relative proportion of the two bases.¹

As regards practical details the following was the general routine. From 25 to 45 grammes of the powdered sandstone was extracted by boiling with strong HCl —about 40 cc. of acid being used in each case. The sand was then washed out with boiling (distilled) water and the finer debris separated by filtration. Soluble silica was then separated in the usual way, and H_2S passed through the hot acid solution for over an hour. What preecipitate formed was filtered off and repeatedly

¹ These residues gave cobalt and nickel oxides in the proportion of 64 to 36.

washed with H_2S solution. The filter with the precipitate, after drying, was burned in a porcelain crucible and the residue strongly ignited for a long time. The copper in this residue evidently being converted into oxide dissolved completely in strong HCl on warming. To the solution ammonia in excess was then added, and any precipitated lead filtered off. In every instance the amount of copper present was sufficient to give a very perceptible blue colouration in about 30cc. of solution. This solution was then carefully neutralised, and the amount of copper oxide in it determined colorimetrically by potassium ferrocyanide (which strikes a fine red with the minutest traces of copper) and a standard copper solution. It was found that the hydrochloric acid contained a very minute trace of copper. Two concordant determinations made by evaporating separately, 40 cc. and 160 cc. of the acid, gave as nearly as possible 1 part of acid in 1,500,000 parts by weight of acid. A specimen of "pure" HNO_3 gave a result indicating the presence of about five times as much copper in an equal quantity. HNO_3 was accordingly not used. The quantity of CuO in 40 cc. of hydrochloric acid failed to strike a blue colouration with ammonia, though a decided reaction was obtained with potassium ferrocyanide.

From the quantity of copper oxide obtained in a given specimen of sandstone, the amount corresponding to the acid used was deducted—it amounted to only $\frac{1}{40}$ of a milligramme—and in every instance a relatively very substantial balance in favour of the sandstone was obtained. By way of test the following experiment was made. A known weight of the sandstone giving the lowest result (Spynie) was treated as already described, when a result after correction for the acid, was obtained indicating an amount of CuO equal to 1 in 142,000 parts of sandstone. A similar weight of the same sandstone was extracted with the same acid after redistillation—in that case presumably copper free—when a result indicating 1 in 160,000 parts was obtained. The difference may reasonably be taken as falling within the range of estimational error and as indicating that the correction was practically sufficient.

The presence of lead was ascertained in quite a number of cases, but as the acid also showed a minute trace of lead—which was not estimated—the results could not be set down with absolute accuracy. Its presence when using redistilled acid was however ascertained in the following cases, in which of course the copper, which is also set down—was also determined after use of a copper-free acid:—

Specimen of Sandstone.	Quantity taken.	CuO Absolute amount found.	CuO Relative amount found.	PbO
Rosebrae (U.O.R.) . . .	29.4 grms.	.35 mgrms.	$\frac{1}{84000}$	5 mgrms. PbSO ₄
Spynie (Trias.) . . .	32.	.2	$\frac{1}{180000}$	present
Cuttieshillock Pebble band with MnO ₂ and pebbles up to $\frac{3}{8}$ ' Diam.	57.4	1.1	$\frac{1}{52000}$	present
Cummingston (Trias.) with CaF ₂	32.6	.35	$\frac{1}{93000}$	present

In the case of the last, lead was present both in the filtrate and as sulphate in the finer debris separated by filtration, as the latter was observed to darken in colour on exposure to H₂S. Again in a specimen from the L.O.R. at Spey Bridge a quantity of lead (PbO = $\frac{1}{50000}$) was also obtained far in excess of anything that could be expected from the acid used. In fact the precipitate in this case was the bulkiest of the whole series.

The quantities of CuO obtained over all range (after correction for acid which was indeed hardly necessary) from $\frac{1}{38000}$ at Spey Bridge to $\frac{1}{180000}$ at Spynie—the average over all being $\frac{1}{77000}$

After separation of the copper, lead, &c., iron and alumina were separated after oxidation and neutralisation in some cases, by barium carbonate in other cases, from the boiling solution by sodium acetate, and the nickel and cobalt precipitated by passing H₂S through the filtrate acidified with acetic acid. The precipitate was collected, washed, dried, and ignited; and if sodium acetate had been used redissolved in strong HCl, and H₂S again passed through the acid solution (as some specimens of that re-agent were found to contain traces of copper and lead), any precipitate that might form filtered off, and the nickel and cobalt re-precipitated in the filtrate. In every instance a deep *brown* colouration of the filtrate was obtained. On standing a considerable precipitate was in most instances eventually thrown down. This was collected, washed, ignited and weighed, and the result taken as oxide calculated into parts per thousand. As regards exactness of determination this series is not to be compared with the determinations of the copper. Nickel, even in large quantities, is a notoriously fickle substance to estimate with precision, and it is premised that while some of the determinations may be too high from imperfect washing, others are just as likely to be too low from loss from the relative solubility of nickel sulphide. The quantities obtained range from $\frac{1}{30000}$ at Oakbrae and Miltonbrae in the U.O.R. division to $\frac{1}{19000}$ in the Pebble band at Cuttieshillock. Over all an average of $\frac{1}{19800}$ was obtained.

Indications of the presence of other metals of the H_2S group have been observed from time to time, but as these could not be investigated, at least in the same sample without risk of upsetting the copper determinations, they were for the time being neglected. It is also possible that the nickel and cobalt residues may contain traces of zinc.¹

From the method of extraction it will be inferred that these traces of the heavy metals occur as interstitial substances in the sandstones. It has also been found that they generally, though apparently not invariably, occur in greatest quantity in association with peroxide of manganese. They are therefore, in all probability, secondary infiltration products, and, so far as evidence has yet accumulated, I am inclined to ascribe their presence to perfiltration of sea water or other highly concentrated natural water. In the former, of course, all these metals, and many more besides, have been found. In support of the explanation now given I have also to record the presence of soluble sulphates and chlorides in eleven out of fourteen specimens of sandstone of the area, examined by me in this relation several years ago. On the same hypothesis, the manganese stains and manganese nodules would fall into line with the manganese nodules of the deep sea deposits, which have also been found to contain traces of copper, nickel and cobalt, etc. But manifestly many practical, as well as theoretical, details will have to be settled before a final opinion can be given on the questions raised.

The presence of traces of the heavy metals diffused through sedimentary strata is of theoretical interest in relation to the explanation of mineral veins. In this connection it is worthy of note that the only mineral veins of the area, so far as I am aware, are of copper sulphide at Nairn and of lead sulphide at Lossiemouth. Both of the metals indicated are here shown to occur in traces diffused through the local sandstones.

In conclusion, it has to be noted that the fact of the occurrence of traces of the heavy metals diffused through sedimentary strata was made known by F. von Sandberger² many years ago, but the present paper, so far as I am aware, contains the first record of their presence in any series of British rocks.

¹ No zinc was found.

² Untersuchungen über Erzgänge.

